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16. ABSTRACT

Precipitation samples were collected for approximately 90 daily and 50 weekly sampling periods at Finley Farm, near Raleigh, NC from August 1981 through October 1982. Ten wet-deposition samplers were used. 4 samplers were operated for daily sampling, and 6 samplers were operated for weekly-sampling periods. This design was used to determine if:1) collection efficiences of precipitation are affected by small distances between the Universal precipitation gage and collector; 2) measurable evaporation loss occurs and 3) pH and specific conductance of precipitation vary significantly within small distances.

Average collection efficiencies were 97% for weekly sampling periods compared with the rain gage. Collection efficiencies were examined by seasons and precipitation volume. Neither factor significantly affected collection efficiency. No evaporation loss was found by comparing daily sampling to weekly sampling at the collection site, which was classified as a subtropical climate. Correlation coefficients for pH and specific conductance of daily samples and weekly samples ranged from 0.83 to 0.99.

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JOURNAL ARTICLE

COMPARISON OF DAILY AND WEEKLY PRECIPITATION SAMPLING EFFICIENCES USING AUTOMATIC COLLECTORS

L. J. SCHRODER

U.S. Geological Survey, P.O. Box 25046, MS 407, Lakewood, CO 80225, U.S.A.

R. A. LINTHURST

Department of Botany, North Carolina State University, Raleigh, NC 37650, U.S.A.

J. E. ELLSON

U.S. Department of Agriculture, North Carolina State University, Raleigh, NC 37650, U.S.A.

and

S. F. VOZZO

Department of Botany, North Carolina State University, Raleigh, NC 37650, U.S.A.

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Abstract. Precipitation samples were collected for approximately 90 daily and 50 weekly sampling periods at Finley Farm, near Raleigh, North Carolina from August 1981 through October 1982. Ten wet-deposition samplers (AEROCHEM METRICS MODEL 301) were used; 4 samplers were operated for daily sampling, and 6 samplers were operated for weekly-sampling periods. This design was used to determine if: (1) collection efficiences of precipitation are affected by small distances between the Universal (Belfort) precipitation gage and collector; (2) measurable evaporation loss occurs and (3) pH and specific conductance of precipitation vary significantly within small distances.

Average collection efficiencies were 97% for weekly sampling periods compared with the rain gage. Collection efficiencies were examined by seasons and precipitation volume. Neither factor significantly affected collection efficiency. No evaporation loss was found by comparing daily sampling to weekly sampling at the collection site, which was classified as a subtropical climate. Correlation coefficients for pH and specific conductance of daily samples and weekly samples ranged from 0.83 to 0.99.

1. Introduction

The National Atmospheric Deposition Program (NADP) was organized in 1977 to provide information on spatial and temporal trends of atmospheric deposition. The AEROCHEM METRICS MODEL 301 (ACM) collectors based on the Health and Safety Laboratory (HASL) design (Volchock and Graveson, 1976) were choosen by the NADP (Cowling, 1978; Bigelow, 1982). More than 100 of these automatic collectors were installed across the country to obtain weekly wet-deposition samples for the NADP.

Average collection efficiences for these collectors have been shown to be less than 100% by comparing the volume of precipitation recorded at the Universal (Belfort) gage to the volume of precipitation in the collection bucket (Bogen *et al.*, 1980; Galloway and Likens, 1976; and DePena *et al.*, 1980). Goodison (1978) has found that Alter-shield Universal precipitation gage efficiencies are effected by wind speed and under measures

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true snowfall by 30% at wind speeds exceeding 1 m s^{-1}. However, only rain events occured during this study. It is assumed that the rain gage and the collector are located near each other and remain at the initial installation.

This study was designed to determine if: (1) Collection efficiencies for wet deposition are affected by small distances between the gage and collector; (2) evaporation loss occurs in weekly sample collectors; and (3) pH and specific conductance of precipitation vary significantly within small distances.

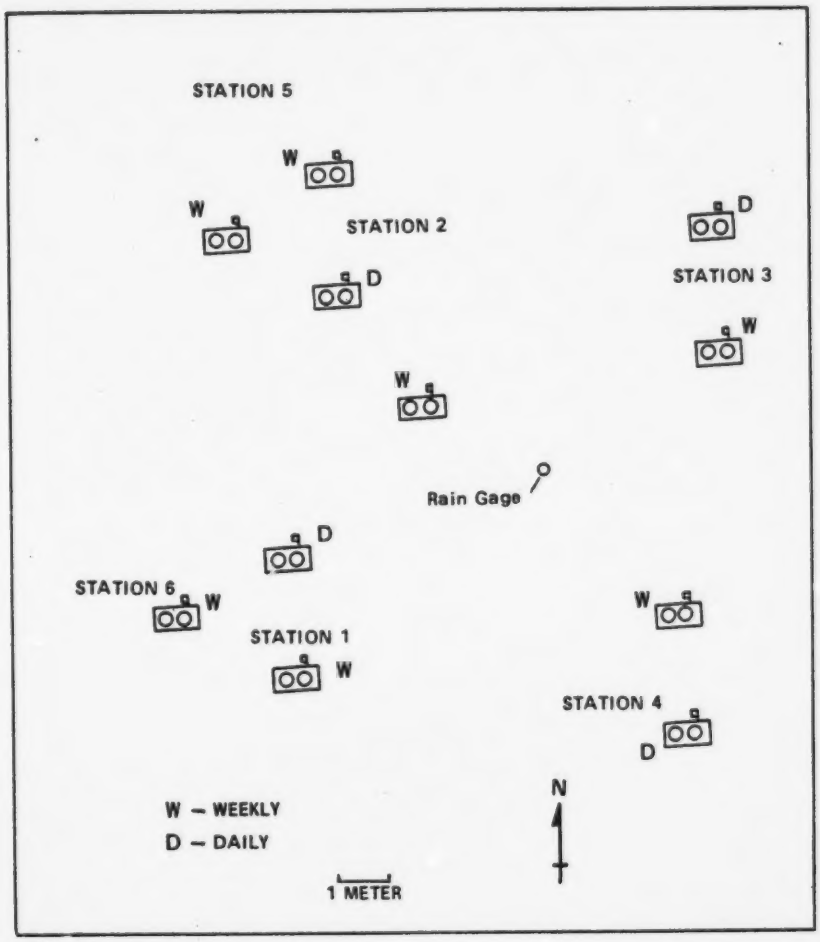

Fig. 1. Collection stations at the sampling site, Finley Farm, Raleigh, North Carolina.

2. Site Description and Collector Configuration

NADP site 344160 has been operating at Finley Farm, Raleigh, N.C. since 1977. Ten ACM collectors are operated there by the U.S. Department of Agriculture in cooperation with the U.S. Geological Survey. Four collectors sample daily precipitation and 6 collectors sample weekly precipitation.

Collectors are located approximately 2.3 km southeast of the airport at Raleigh, N.C. Each collector is set at ground level, with the collection vessel 1.5 m above the land surface. Elevation of the site is 122 m above sea level; mean annual precipitation is 1.17 m (Hardy and Hardy, 1971). Precipitation usually is rain produced by convective storms; maximum precipitation is recorded in July. Maximum evaporation is recorded in June. Field crops are planted and harvested on two adjacent sides of the site. The climate is classified as subtropical, using the Koppen (1931) system.

Four pairs of collectors are designated stations 1 to 4 (Figure 1). These four stations form a square with 8-m sides. The two collectors at each station are 2 m apart, with one collector sampling weekly and the other sampling daily. Station 5 is 76 m from the center of the square; station 6 is 104 m from the center of the square; both are collecting weekly samples. The Universal rain gage is located near the center of the square to measure daily precipitation and is used as the primary standard as required by NADP protocol (Bigelow, 1982). Opening and closing of all collectors comprising stations 1 to 4 are monitored, using a multichannel recorder.

3. Sampling Protocols

NADP collection protocol was followed for weekly samples; it requires that wet-deposition samples be removed from the collector at 9:00 a.m. local time each Tuesday, unless it is raining or snowing at the time. The wet-deposition sample is removed as soon as possible after cessation of precipitation, but no later than 12:00 midnight local time on Tuesday. Daily samples were collected, using the Electric Power Research Institute (EPRI) protocol for definition of an individual storm (Topol, 1982). EPRI collection protocol requires that samples are removed from the collectors 6 hr after the cessation of precipitation. If it is raining or snowing at the end of the normal working day at the site, samples are removed from the collectors the next morning. Daily samples on Tuesday were removed from the collectors at the same time as NADP samples. This daily-sampling protocol was chosen because EPRI has a wet/dry collector at the study site, and Pack (1980) has shown that EPRI and the Multi-State Atmospheric Power Production Pollution Study (MAP3S) networks provide comparable data.

After either EPRI or NADP sampling protocols have been met, collection vessels are removed from the collector and weighed to obtain the quantity of precipitation collected. This quantity is then compared to the precipitation amount recorded by the Universal rain-gage to obtain collection efficiency, which is defined in this study as volume collected, multiplied by 100, divided by the calculated volume expected from the rain

TABLE I

Collection efficiency (%) of daily sampling collectors by precipitation quantity from August 1981, through October 1982, at Finley Farm, Raleigh, North Carolina [cm, centimeter; CI, 95% confidence interval; N, number of samples]

Precipitation quantity (cm)		Station number			
		1	2	3	4
0.13 to 1.27	Mean	99	99	99	97
	CI	4.5	4.9	4.3	4.4
	N	55	57	53	57
1.28 to 2.54	Mean	98	98	96	96
	CI	1.6	1.6	1.7	2.4
	N	23	23	21	23
>2.54	Mean	97	97	95	95
	CI	1.6	1.3	2.3	2.2
	N	13	13	11	13

TABLE II

Collection efficiency (%) of weekly sampling collectors by precipitation quantity from August 1981 through October 1982, at Finley Farm, Raleigh, North Carolina [cm, centimeter; CI, 95% confidence interval; N, number of samples]

Precipitation quantity (cm)		Station number					
		1	2	3	4	5	6
0.13 to 1.27	Mean	106	102	103	103	91	96
	CI	6.3	6.5	6.0	6.0	6.9	8.4
	N	20	19	18	18	18	14
1.28 to 2.54	Mean	98	98	95	98	92	97
	CI	3.1	3.1	4.3	3.0	4.9	3.3
	N	10	10	10	11	10	9
>2.54	Mean	99	96	97	96	94	97
	CI	2.2	1.8	1.7	1.7	3.3	2.9
	N	19	19	22	22	22	16

gage. Immediately after weighing the collection vessel, a portion of the sample is removed to measure pH and specific conductance.

4. Discussion and Results

Replicate precipitation samples were collected for 14 mo at the site from August, 1981 through October, 1982. During this period, 93 events (as defined by EPRI protocol) deposited 0.13 cm or more precipitation. Events resulting in less than 0.13 cm

TABLE III

Collection efficiencies (%) of paired daily and weekly sampling collectors by season from August 1981, through October 1982, at Finley Farm, Raleigh, North Carolina [CI, 95% confidence interval; N, number of samples]

Sampling season		Station number							
		1		2		3		4	
		Daily	Weekly	Daily	Weekly	Daily	Weekly	Daily	Weekly
Fall	Mean	94	96	96	95	94	96	94	96
	CI	4.6	4.2	5.5	5.5	6.5	4.2	5.5	5.5
	N	18	8	18	8	18	8	18	8
Winter	Mean	98	100	98	98	96	98	96	98
	CI	4.0	6.8	4.0	7.4	4.5	7.4	4.4	5.3
	N	24	12	24	12	23	12	24	12
Spring	Mean	98	99	101	98	98	93	96	98
	CI	3.6	4.7	4.0	3.3	4.6	6.2	4.4	5.3
	N	24	11	24	9	18	8	24	11
Summer	Mean	99	106	103	104	100	105	98	104
	CI	3.8	6.5	4.3	4.5	5.6	5.1	5.1	4.9
	N	21	13	21	12	21	12	21	13

precipitation were excluded from the daily sample data. For 0.13 cm precipitation, 91 g of moisture would be obtained at 100% collection efficiency. Results of collection efficiency of the wet collectors are given in Tables I and II by rainfall quantity. Average catch efficiency of daily wet collectors is 97 ± 12%. These efficiencies are virtually the same as the efficiencies reported by Bogen *et al.* (1980), and greater than efficiencies reported by Galloway and Likens (1976). Bogen *et al.* reported a collection efficiency of 96 ± 10% for monthly sampling in a tropical climate. Galloway and Likens (1976) reported a mean collection efficiency of 94% for rain and 86% for snow. Therefore, average collection efficiency for daily and weekly sampling from this study, and monthly sampling by Bogen *et al.* (1980) are within the estimated errors of the averages and are the same for all three sampling records, as determined by comparing the ratio of the sampling variance.

Collection efficiencies of the weekly collectors include precipitation quantities that are less than 0.13 cm. These small quantities are difficult to measure accurately using the weighing rain gage at the collection site. Accumulation of small quantities in the total precipitation for the week may account for the greater than 100% mean collection efficiencies shown in Table II for precipitation quantities in the 0.13 to 1.27 cm range for station 1 through 4. This possibility does not explain the lesser efficiencies for stations 5 and 6. It appears that the distance from the rain gage to these stations causes lesser collection efficiencies for precipitation quantities from 0.13 cm to 1.27 cm. Confidence limits from station 5 are 89.4 and 96.6%. Confidence limits from station 6 are 91.8 and 100.2%. Both stations 5 and 6 confidence intervals overlap the overall

weekly sampling confidence intervals, but station 5 does not include 100%. This indicates that the rain gage and collector may be 76 m apart for good correlation but the correlation is less if they are 100 m apart.

Collection efficiencies for the paired collectors at stations 1 through 4 were examined by season (fall, winter, spring, summer) to determine if measurable evaporation occurred in the weekly sampling collectors. As shown in Table III, collection efficiencies for weekly sampling collectors are generally equal to or greater than collection efficiencies for daily-sampling collectors. The daily measurements at each station were totaled to provide a calculated weekly collection efficiency. The hypothesis that the calculated weekly collection efficiencies equals the measured weekly collection efficiencies was tested using a paired-t test. Hypothesis can be accepted for Stations 1, 3 and 4 at $\alpha = 0.05$. Hypothesis can not be accepted, at $\alpha = 0.05$, for Station 2 but is accepted at $\alpha = 0.01$. If evaporation is occurring in the weekly collectors, the loss is not sufficient to be distinguishable. This is true even for fall and summer seasons, when ambient temperature reaches 32 °C at least 40 or more times (Hardy and Hardy, 1971).

Hales (1978), Peden and Skowron (1978), and Schriner (1979), indicated that chemical changes or alterations are possible, when sampling is conducted for collection periods longer than daily sampling. Chemical analyses of both daily and weekly samples collected during this study will be completed at a later date and made available. However, comparison of pH and specific conductance for daily and weekly sampling

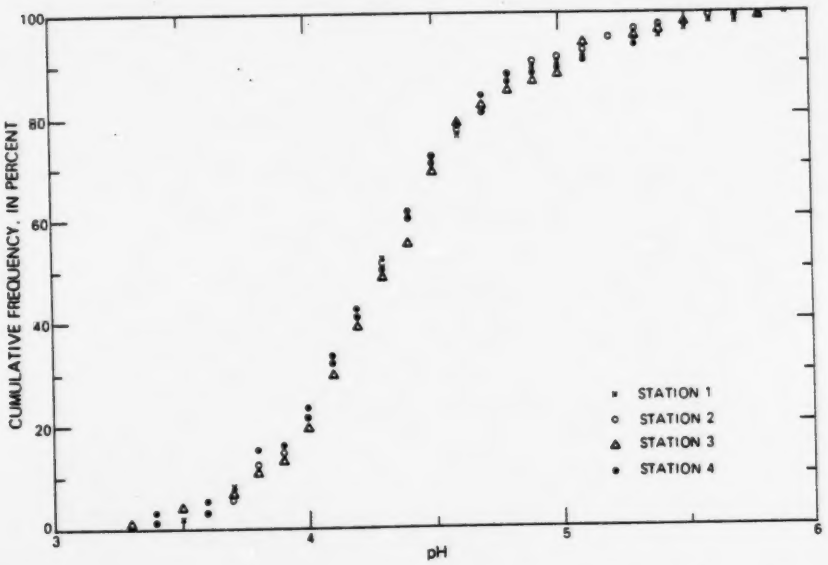

Fig. 2. Daily sample pH from August 1981, through October 1982, at Finley Farm, Raleigh, North Carolina.

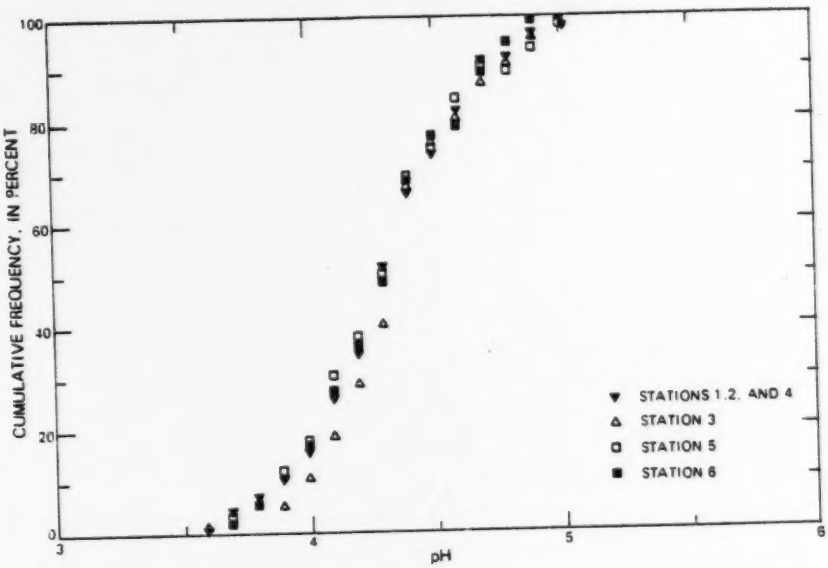

Fig. 3. Weekly sample pH from August 1981, through October 1982, at Finley Farm, Raleigh, North Carolina.
Due to similarity of data, only one symbol is used for stations 1, 2 and 4.

is shown on Figures 2 through 5. Median pH at each daily and weekly sampling collector is 4.4.

However, weekly samples mask daily sample extremes for both pH and specific conductance. Cumulative frequency plots for pH in Figure 2 show many daily samples with a pH greater than 5.1, or a pH less than 3.5. Weekly sample frequency plots for pH encompassing the same time-frame (Figure 3) contain no samples with pH less than 3.5 or greater then 5.1. Comparison of Figures 4 and 5 for specific conductance also demonstrates the masking of daily sampling extremes. No weekly samples occured with specific conductance less than 5 μS cm^{-1}, but about 5% of the daily samples have specific conductance less than 5 μS cm^{-1}. Mean specific-conductance is 27.8 μS cm^{-1} for daily-samples, and 25.7 μS cm^{-1} for weekly smples. The pH and specific conductance data indicate that gross changes are not occuring with collection periods of 1 week, but selected chemical changes may be occurring.

Correlation coefficients for pH and specific conductance by sampling stations are shown in Tables IV and V. Daily sample correlation coefficients are greater than 0.88 for pH, and greater than 0.98 for specific conductance. Weekly sample coefficients are greater than 0.90 for pH and specific conductance unless station 6 data are used in the comparison. However, the lowest correlation coefficient for all station comparisons is 0.791, resulting from comparing pH between stations 3 and 6. These significant

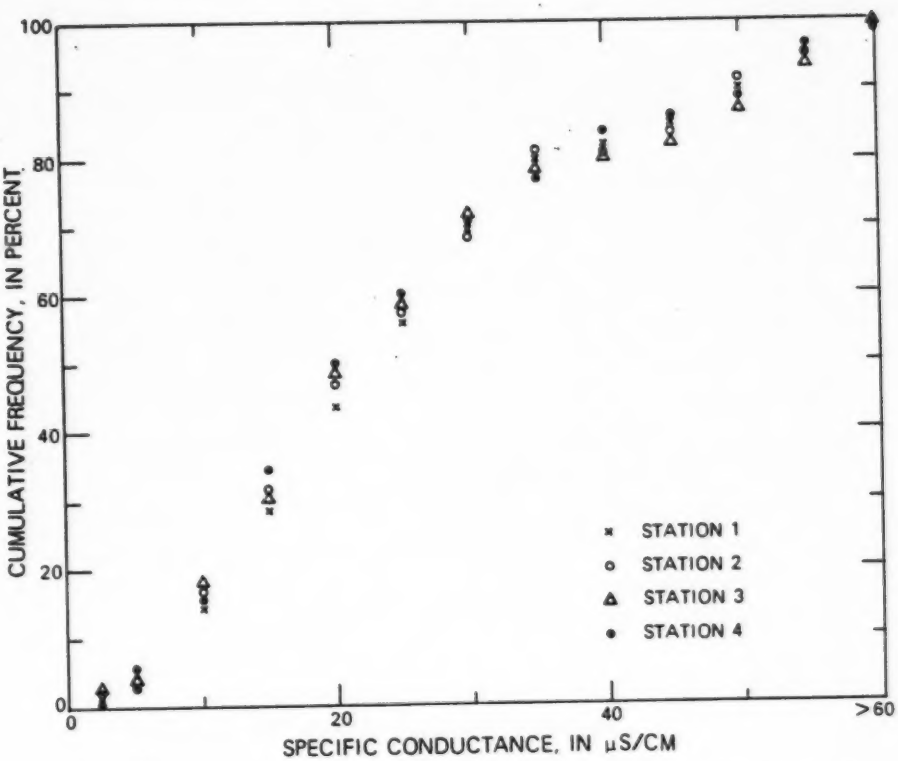

Fig. 4. Daily sample specific conductance from August 1981, through October 1982, at Finley Farm, Raleigh, North Carolina.

TABLE IV

Correlation coefficients for pH and specific conductance of daily samples at Finley Farm, Raleigh, North Carolina

Station identification	Number of comparisons	Correlation coefficients	
		pH	Specific conductance
1 to 2	92	0.984	0.991
1 to 3	85	0.900	0.989
1 to 4	92	0.882	0.983
2 to 3	85	0.932	0.993
2 to 4	92	0.900	0.989
3 to 4	85	0.944	0.988

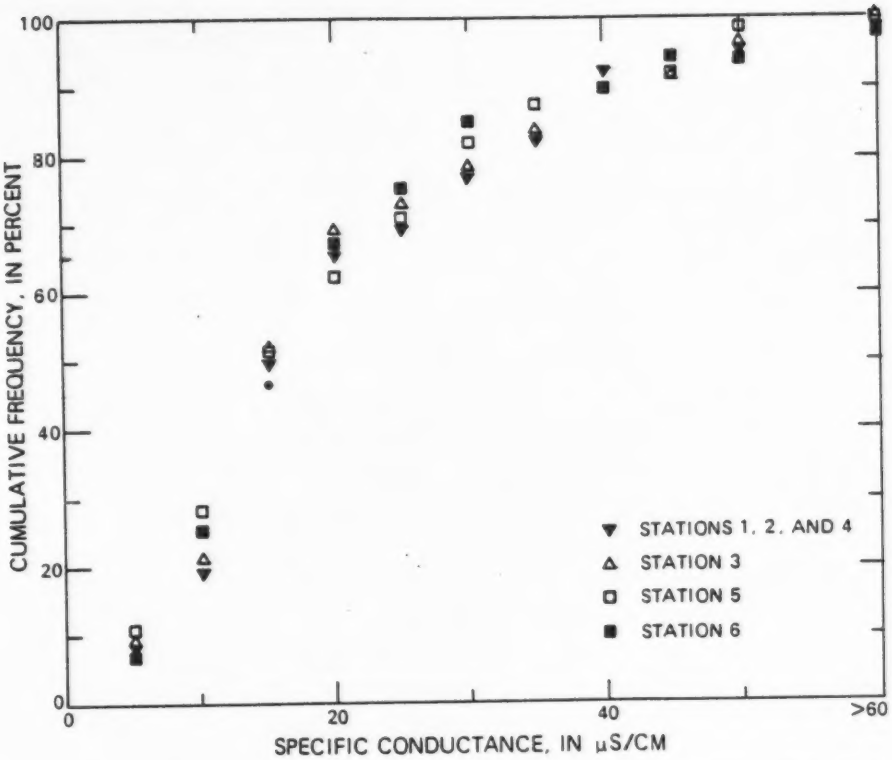

Fig. 5. Weekly sample specific conductance from August 1981, through October 1982, at Finley Farm, Raleigh, North Carolina. Due to similarity of data, only one symbol is used for stations 1, 2, and 4.

correlations plus similar means obtained at each station indicate that pH and specific conductance of precipitation is virtually uniform, as measured by collectors as much as 175 m apart.

5. Conclusions

Wet-deposition collectors based on the HASL design were used for daily and weekly sampling periods. Collection efficiencies were similar for 9 of the 10 collectors. Collection efficiency at station 5 indicates that a collector 76 m from the rain gage has the same collection efficiency as collectors only a few meters from the gage. The collector at station 6, 104 m from the rain gage may not have the same collection efficiency as a collector closer to the gage. Evaporation losses in ACM collectors based on the HASL design are not a problem in subtropical climate, even during the summer. Correlation of pH and specific-conductance data from station to station at the sampling site

TABLE V

Correlation coefficients for pH and specific conductance of weekly samples at Finley Farm, Raleigh, North Carolina

Station identification	Number of comparisons	Correlation coefficients	
		pH	Specific conductance
1 to 2	41	0.975	0.973
1 to 3	43	0.925	0.928
1 to 4	45	0.969	0.968
1 to 5	45	0.945	0.930
1 to 6	29	0.827	0.940
2 to 3	41	0.941	0.964
2 to 4	43	0.985	0.997
2 to 5	41	0.969	0.956
2 to 6	29	0.866	0.972
3 to 4	43	0.956	0.930
3 to 5	41	0.950	0.941
3 to 6	29	0.791	0.922
4 to 5	41	0.971	0.957
4 to 6	29	0.881	0.980
5 to 6	29	0.874	0.960

indicates that these parameters are virtually uniform as measured by collectors as much as 175 m apart even though the collection efficiencies may be different. The pH and specific-conductance data indicate that gross chemical changes are not occurring with collection periods of 1 week, but do not eliminate the possibility that selected chemical changes may be occuring.

Information obtained from this study would be applicable to NADP sites that are located in subtropical or tropical climates. This would include much of southeastern United States and may include other sites that receive precipitation as rain only. Properly maintained and operated wet-deposition collectors can achieve nearly 100% collection efficiency if the event is greater than 0.13 cm of rain.

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